Morphological and Properties Characterization of Melt-Spun Poly(Lactic Acid)/Cellulose Nanowhiskers Fibers: Effect of Filler Content

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Abstract:

The production of poly(lactic acid) (PLA)/cellulose nanowhiskers (CNW) bionanocomposites represents an efficient route to enlarge their application in many industrial fields, with the possibility to control the properties by filler content adjustment. In this work, fibers yarns of PLA and PLA/CNW filled at 1 and 3 wt.% were prepared by melt spinning in the presence of PLA-*grafted*-maleic anhydride (PLA-*g*-MA) used as the compatibilizer. The study aimed at investigating the influence of filler content on the morphology and properties of PLA/CNW bionanocomposites fibers. The results showed that adding only 1 wt% of CNW in PLA in the presence of compatibilizer improved the morphology and the thermal stability of the bionanocomposite fibers than those filled with 3 wt%, while the tensile properties were almost comparable to the neat PLA.

Keywords: Poly(lactic acid); Cellulose nanowhiskers; Bionanocomposites; Melt spinning; Fibers

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Results and Discussion

❖ Morphological analysis of PLA and PLA bionanocomposite fibers :

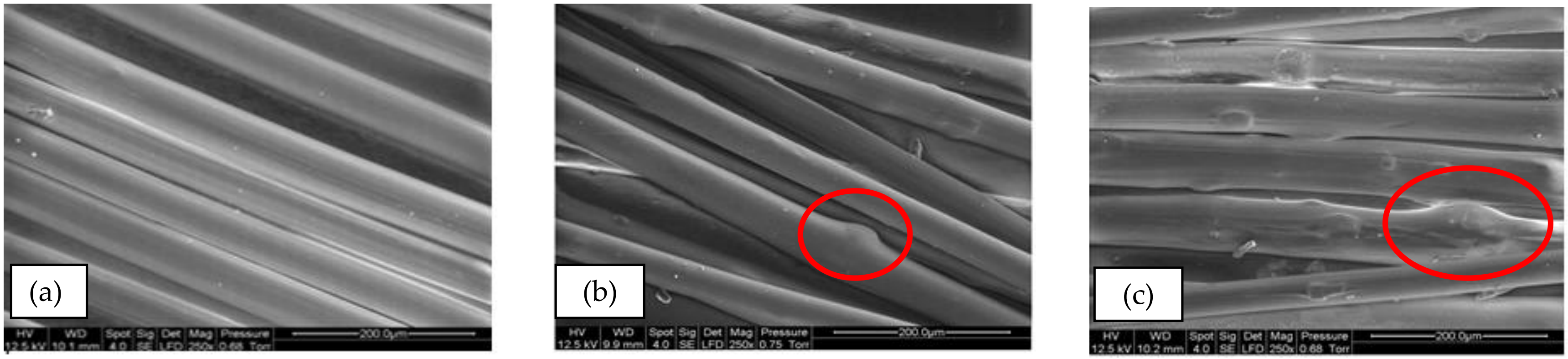

Figure 1. SEM images of the external surface fibers of: **a)** neat PLA and PLA/PLA-*g*-MA/CNW bionanocomposites **b)**: 1 wt% and **c)**: 3 wt%. **250 X**

(a): A smooth and regular surface with a good cylinder-shape for neat PLA.

(b): A small bulging surface of PLA/PLA-*g*-MA/CNW1 filaments due probably to aggregations of nanocrystals (CNW), being however more pronounced at 3 wt% **(c)**.

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❖Morphological analysis of PLA and PLA bionanocomposite fibers :

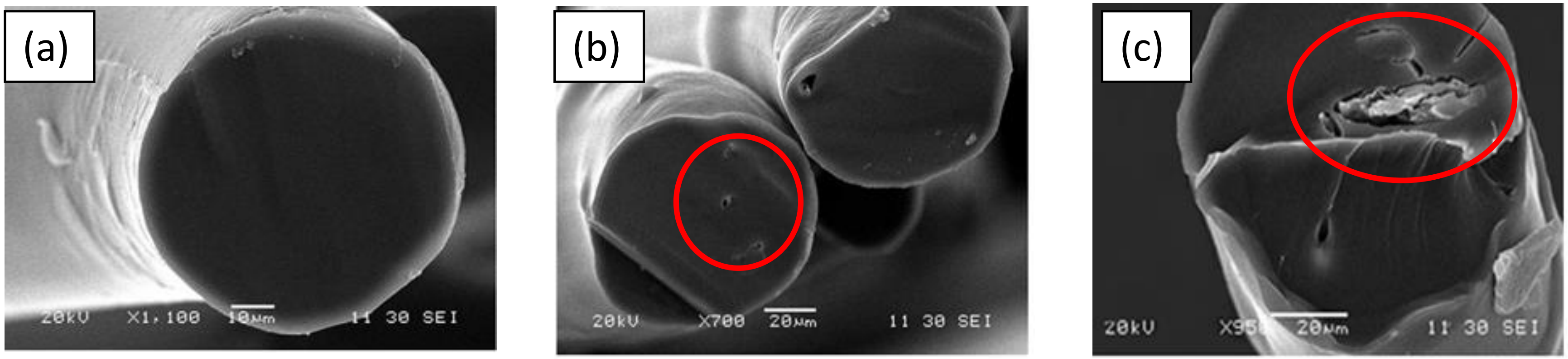

Figure 2. SEM images of the cross-sectional surface fibers of: **a)** neat PLA and PLA/PLA-*g*-MA/CNW bionanocomposites **b)**: 1 wt% and **c)**: 3 wt%.

- **(a)** No surface defects.
- **(b)** Presence of smaller size domains of CNW at 1 wt% than 3 wt% which is characterized by formation of aggregates **(c)**.

❖ Tensile properties :

Table 1. Values of Young's modulus, tensile strength at break and (%) elongation at break of neat PLA and PLA/CNW bionanocomposite fibers.

Samples	Young's modulus (MPa)	Tensile strength at break (MPa)	Elongation at break (%)
PLA	2510±158	92.2±5.4	77.7±7.3
PLA/PLA-g-MA/CNW1	2334±99	83.9±3.8	91.6±4.9
PLA/PLA-g-MA/CNW3	930±92	22.2±1.9	19.0±3.5

- A very slight decrease in Young's Modulus at 1 wt% filler content compared to neat PLA.
- At 3 wt%, there is a dramatic decrease in Young's modulus due probably to aggregates formation.
- Similar trend is also observed for tensile strength of PLA /CNW biocomposites.
- Conversely, an increase in elongation at break is noticed at 1 wt% filler content , which is more than that of neat PLA.
- These results are consistent with morphological data.

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❖ Thermal stability:

Table 2. TGA data of neat PLA and PLA/CNW bionanocomposite fibers.

Samples	T_{onset} (°C)	T_{mrd} (°C)	Char at 500°C (%)
PLA	311	362	0.6
PLA/ PLA-g-MA/CNW1	326	369	0.1
PLA/PLA-g-MA/CNW3	320	367	1.3

- Incorporation of CNW increases the thermal stability of PLA biocomposites however, more pronounced at 1 wt%.
- Similar trend is also observed for the temperature at maximum rate of degradation (T_{mrd}).
- The increase in thermal stability at 1 wt% is probably attributed to a better dispersion of the filler in the matrix.

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❖ DSC analysis

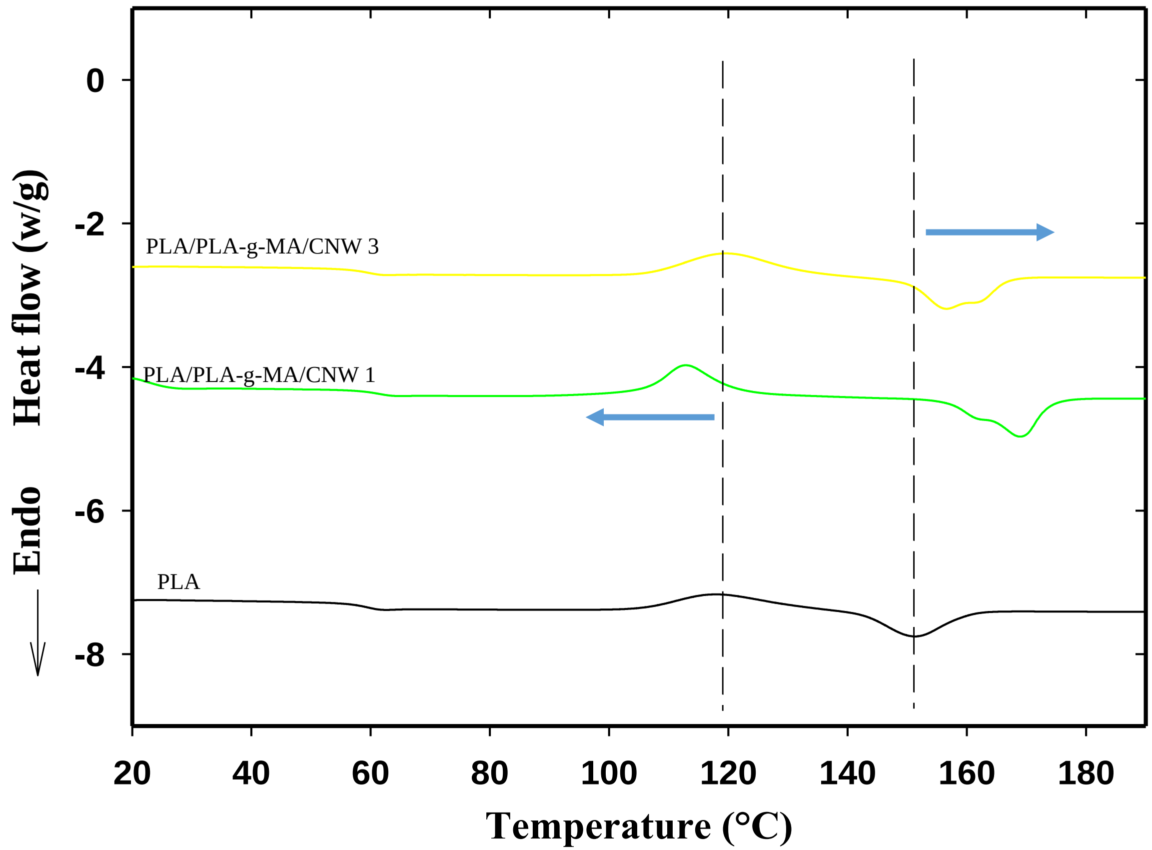

Figure 3. DSC thermograms of PLA and PLA bionanocomposites (Second heating).

- Increase in Tm of PLA bionanocomposites due to thickening of crystallites.
- Decrease in Tc indicates an increase in crystallization rate meaning that CNW may act as nucleating agent.

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Conclusions

From this study, it can be concluded the following:

- Up to 3 wt%, it is possible to elaborate by melt-spinning PLA/CNW fibers rather than electro-spinning process keeping mainly the functional properties of the fibers.
- All results indicated clearly that better fibers performances were achieved by adding CNW at 1 wt% in PLA compared to 3 wt%.
- Indeed a better morphological surface was observed at 1 wt% than 3 wt% in PLA matrix and almost 18% increase in elongation at break was obtained compared to neat PLA.
- In addition, the onset degradation temperature was increased by 15°C at 1 wt%, which indicates a better thermal stability.
- Finally, the study showed that CNW is a promising reinforcement for biodegradable polymers such as PLA.

Supplementary Materials

STEP1: PREPARATION OF PLA/CELLULOSE BIONANOCOMPOSITES BY A TWIN-SCREW EXTRUDEUR

Table 3. Processing parameters used in the extrusion step

Screw speed (rpm)	Temperature (°C)				
	T_1	T_2	T_3	T_4	T_5
100	160	170	180	185	190

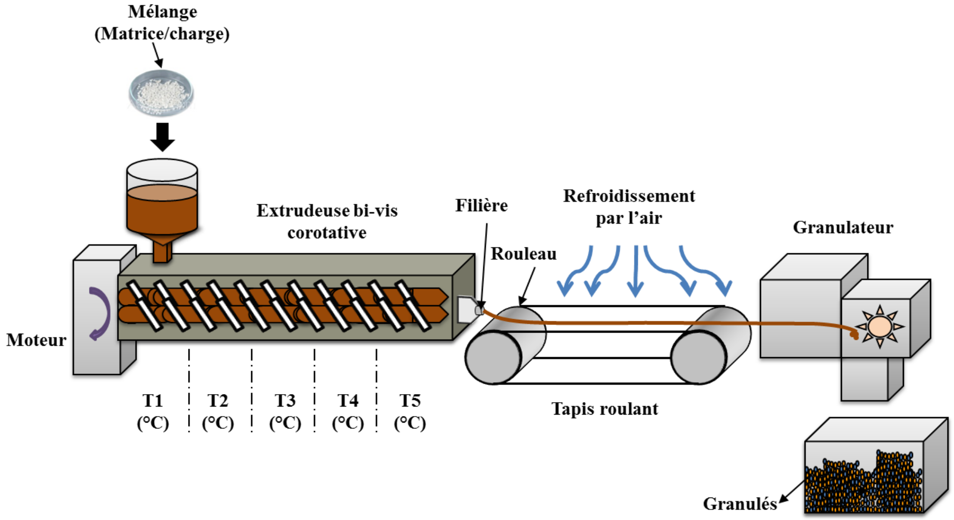

Figure 4. A twin-extrusion line to elaborate PLA and PLA/cellulose bionanocomposites granules

Table 4. Summary of PLA multifilament yarns code and compositions.

PLA (wt%)	PLA-g-MA (wt%)	Fillers (wt%)	Formulations
100	0	0	PLA
92	7	1	PLA/PLA-g-MA/CNW1
90	7	3	PLA/PLA-g-MA/CNW3

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STEP2: Multifilament spinning conditions and relative diameters

Table 3. Temperature profile in the spinning machine.

Extruder temperature profile (°C)							Roll 1	Roll 2
T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_{R1}	T_{R2}
195	205	210	200	185	185	185	70	90

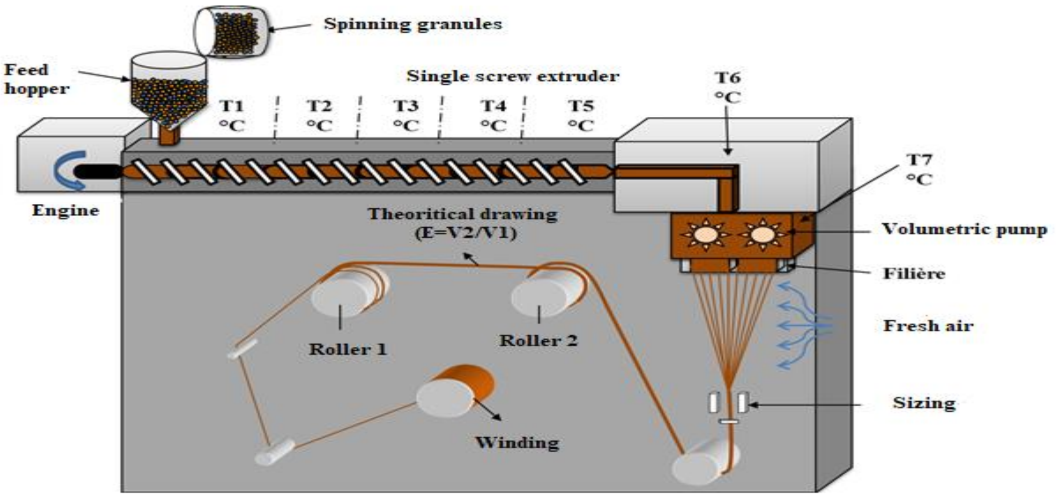

Figure 5. Filament yarns produced by melt spinning process using the Spinboy I machine.

Table 5. Summary of the filaments spinning conditions and their resulting diameters.

Samples	Roll 1 speed (m/min)	Roll 2 speed (m/min)	Draw ratio (DR)	Diameter (µm)
PLA	200	300	1.5	59.4±7
PLA/PLA-g-MA/CNW1	200	300	1.5	59.6±8
PLA/PLA-g-MA/CNW3	200	250	1.25	85.1±10

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